
One possibility for atmosphere CO₂ purification to get climate recovery

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Abstract: Our approach incorporates the possibility of stepwise CO₂ purification in areas of the free atmosphere by spraying of alkaline compounds inside the clouds via an airplane. It causes significantly increases of the CO₂ solubility in rain droplets during their gravitational fall to provide the effective carbon transport to the ground. Presented calculations show a considerable increase of the gas/water interface for perfect CO₂ absorption. This future technology can compensate for annual carbon emission by method application at 0.42% – 0.14% of our planet surface.

Keywords: Atmosphere, Climate Restore, Precipitation, Clouds, CO₂

1. Introduction

Greenhouse gases flowing into the atmosphere cause the ecological problems. On the other hand, the natural ocean of our planet stores great mass of CO₂ due to alkali properties of the ocean water where is $pH \approx 8.3$. Cloud methods for precipitation enhancements have been developed in different countries around the world with wide practice today. We recall that the sum of water vapor and carbon dioxide makes a 95% of the greenhouse gases in a modern atmosphere. Mentioned aspects we used to propose new method for atmosphere purification and further climate recovery.

According to IPCC Fifth Assessment Report the predicted climate trend indicates the global overheating. Nowadays atmospheric carbon dioxide levels are the highest of all known recorded levels [1], and all known natural restore mechanisms have limited capacities in regards to the amount of incoming pollution and also they operate within specific time constants according to [2]. The purification of Earth's free atmosphere is novel and very difficult global problem to analyze and solution for today [3]. The idea of weather/climate modification by precipitation enhancement was generated by Langmuir in [4]. Background studies were developed later for clouds and precipitation enhancement in [5]. The most popular technologies today for precipitation enhancement are those that involve the sprinkling of hygroscopic particles or glacial substances into 'warm' or 'cold' clouds according to [6 - 8].

Our approach incorporates the possibility of stepwise CO₂ purification in two stages to be conducted in areas of the free atmosphere. The first stage involves spraying of alkaline compounds, such as KOH and etc., inside the cloud via an airplane to increase the pH in cloud droplets. The alkaline reagents significantly increase the solubility of CO₂ in water, however rain droplets become saturated by atmospheric CO₂ during their gravitational fall. Due to the small CO₂ concentration in air the probability of collision between water droplets and CO₂ molecules is low in cloud media, so modified cloud droplets spend their alkali capacity later during rain. The rainy droplets provide the transport of CO₂ from the atmosphere to the ground and further more to soil, ground water and plants. In addition to it, the special acoustic devices can be utilized to accelerate the coalescence of water droplets in modified clouds as possible second stage of proposed method according to [9 - 10].

2. Analyses

The purification effect strongly correlates with changes of pH level in cloud water. In natural precipitation with neutral pH the concentrations of the dissociated ions are relatively small. There is an established method to describe the insoluble and dissociated portions of the weak acid that remains after attaining the equilibrium of saturation for water by CO₂: $CO_2 + H_2O \rightleftharpoons H_2CO_3$, $H_2CO_3 \rightleftharpoons HCO_3^- + H^+$, and $HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$. Therefore, CO₂ solubility

significantly grows at high pH levels due to increase of H⁺ concentration. The effect was shown by the earlier study [11, 12]; the given data were listed for a cloud with 3 mkg / m³ of NH₃ and the media contains at a pH = 7. The equilibrium concentrations of dissolved and dissociated portions became [H₂CO₃] = C₁ = 0.71 mg/l; [HCO₃⁻] = C₂ = 3.3 mg/l, also [CO₃²⁻] = C₃ = 10⁻³ mg/l. The concentrations of ions [HCO₃⁻] and [CO₃²⁻] increase in 10 and 100 times accordingly by each unit of pH. The ratios of carbon in the first, second and third of the listed compounds are the following: D₁ = 0.1935; D₂ = 0.1967; and D₃ = 0.20. For given water volume U_w the carbon mass can be calculated as:

$$M_c^{U_w}(pH) \approx [0.1935 \cdot C_1 + 0.1967 \cdot C_2(pH) + 0.2 \cdot C_3(pH)] \cdot U_w \quad (1)$$

For instance, a precipitation layer with a height of h_w = 1000 mm covers a unit surface of 1 m², so the corresponding mass of carbon is equivalent to M(10) = N_s(10) · 1000 ≈ 850 g at the pH = 10. Using this approach one can estimate the concentration of CO₂ that is removed from the atmosphere underneath the cloud by precipitation. Let's take the volume of purified air in the atmosphere U_a = 10³ m³ in precipitation, there h_a = 1 km is the altitude of the cloud calculated from the ground for a unit square surface 1 m². The reduced CO₂ concentration C_{a-} was estimated by dissolving the carbon mass in alkaline precipitation under an assumption that the initial concentration of CO₂ was detected underneath the cloud. The molar mass of CO₂ is 44 g, so the share of carbon in it is D₄ = 12/44 = 0.2727. The vertical CO₂ distribution was considered almost uniform [13]. The concentration of removed CO₂ can be estimated as:

$$C_{a-} \approx \frac{0.1935 \cdot C_1 + 0.1967 \cdot C_2(pH) + 0.2 \cdot C_3(pH)}{0.2727} \cdot \frac{h_w}{h_a} \quad (2)$$

For the special case of the complete atmospheric purification in the volume under cloud, we assume that the CO₂ concentration is C_{a-} ≈ 420 ppm. The pH level of the droplet should be increased up to pH=10.3 for complete purification if the cloud located at 1 km above the ground. In general, clouds can be located at various altitudes h_a. For instance in case of the altitude h_a = 6 km the cloud medium should become pH=10.8 to get complete purification in lower area. Let's analyze a chemical approach to introduce KOH into clouds in the form of additional liquid aerosol. There is the dissociation reaction of KOH in water:



The alkali facilitates the dissociation of water, and is used to bring [H⁺] which means the pH, accordingly:



We note that the values of water dissociation constant are taken for two temperatures: K_w = 10⁻¹⁴ at T = 20°C and K_w = 10^{-14.926} at T = 0°C according to [14]. The required KOH mass can be obtained from the known relation:

$$n_{KOH} = K_w / [H^+] = [OH^-] \quad (5)$$

Taking the molar concentrations for KOH and OH from relation (3) we obtain the molar concentration of alkali approximately n_{KOH} = 10⁻⁴ mol/l according to relation (4) then pH = 10. The concentration value N_{KOH} = 56 · 10⁻⁴ g/l = 5.6 · 10⁻⁶ g/cm³ results from n_{KOH} multiplication to the molar mass of KOH. Let's comment upon the data. Suppose in a cloud the liquid water content is W = 1 g/m³, so the air volume 1 m³ contains the 1 cm³ of water, and listed data of n_{KOH} corresponds required alkali mass to air volume 1 m³ to get mentioned pH-level in cloud droplets after evaporation/condensation and restructuring. For example, let the cloud has a volume 1 km³ and W = 1 g/m³, hence the required mass of KOH to add into this cloud should be equal to 5.6 · 10⁻⁶ · 10⁹ · 10⁻³ ≈ 5.6 kg approximately then pH = 10. For example, KOH concentrations as a function of pH is n_{KOH} = 1.7 · 10⁻⁵ g/cm³ then pH=10.5, but pH=10.8 needs n_{KOH} = 3.5 · 10⁻⁵ g/cm³.

We investigate a potential advantage of this precipitation above the flat ocean surface. Due to their small size of rain droplets the falling time must exceed the gas saturation time. The fall velocity V_g(r) can be approximated using the stationary speed of droplet gravitation sedimentation as follows: V_g(r) ≈ √(2rgρ_w/ρ_a), where ρ_a and ρ_w are the densities for air and water respectively, r is a drop radius and g is the acceleration due to gravity. The largest radius has been estimated as 3 - 4 mm due to drop disintegration. However, at the beginning of the precipitation the droplets have grown with radius r ≥ 100 μm due to gravitational sedimentation. The falling time for droplet can be estimated as t_h ≈ h_a / V_g(r) with the initial altitude of h_a = 1 km, these calculations shows for example t_h = 257 sec then r = 1 mm. During the process of CO₂ solubility we can estimate the saturation time t_{aw} for the falling droplets. The steady state concentration depends on the ratio of the air volume U_r for the drop and the area of its surface S_r in a gas flow:

$$t_{aw} \approx \frac{4\pi r^3 / 3}{4\pi r^2 K_{aw}} \approx \frac{r}{3K_{aw}} \quad (6)$$

This process also depends on the gas exchange constant K_{aw} at the gas-water interface and the time of saturation t_{aw}. The constant K_{aw}(V) is a function of the flow speed V ≡ V_g(r). In the previous studies the intensity of CO₂ gas exchange has been measured as a function of the velocity of air flow V over the water surface, according to [15-18]. We employed the following experimental measurements for constants of gas exchange at the gas-liquid interface: K_{aw} = 4 · 10⁻³ cm/s then V = 3 m/s; K_{aw} = 6.4 · 10⁻³ cm/s then V = 5 m/s; also K_{aw} = 1.1 · 10⁻² cm/s if V = 7 m/s. Taking into account the equation (6) and assuming measured constraints for K_{aw}(V) we obtain saturation time t_{aw} = 6 sec for droplet with a typical rain radius r = 1 mm. For the largest droplet with radius r = 3 mm saturation time is t_{aw} = 11 sec and flying time t_h = 148 sec due to velocity V_g = 6.8 m/sec. As t_{aw} << t_h there is enough time for gas saturation during droplet flight to the ground from the altitude h ≥ 1 km.

Next advantage is great increase of the air/water interface in a droplets assemble. Further analysis bases on the Marshall-Palmer approximation [19] for the droplets spectrum for rain as follows:

$$\varphi(r) = n \cdot b \cdot \exp(-br) \quad (7)$$

This empirical formula includes the constant b (cm^{-1}), and the droplet number concentration n (cm^{-3}) that depends on the precipitation rate I , in millimeters per hour. Different types of precipitations can be described by this empirical equation (7) with a 99% experimental coincidence for the parameters b and n using in [20], as follows:

$$\text{drizzle has } a \ b = 57 \cdot I^{0.21} \text{ with } n = 5 \cdot 10^{-3} \cdot I^{0.21};$$

$$\text{rain has } a \ b = 41 \cdot I^{0.21}, \ n = 2 \cdot 10^{-3} \cdot I^{0.21};$$

$$\text{storms have } a \ b = 30 \cdot I^{0.21} \text{ with } n = 5 \cdot 10^{-4} \cdot I^{0.21}.$$

The volume of received water $U_I = AIT\beta$ was calculated as a sum of all of the falling droplets of the water layer I on a ground surface $A = 1 \text{ m}^2$ during $T = 1$ hour (when $I = 3$ mm/hour in calculations below). Here the β coefficient was introduced in order to compare the features for the precipitation types with rate $I = 3; 10$ or 30 mm/hour for drizzle, rain or storm, there are $\beta_1 = 1$, but $\beta_2 = 0.3$, $\beta_3 = 0.1$ also $I_1\beta_1 = I_2\beta_2 = I_3\beta_3$ for all calculations as mentioned in the examples. The radii interval for the complete rain spectrum was calculated over a wide interval $r_m = 0.05 - 3$ mm. Then the percentage of droplets with a radius r_i within the unit water volume can be described with (7) using the ratio

$$q_m = \varphi_m(r_m) / \sum_{r=0.05}^3 \varphi_m(r_m) \quad (8)$$

The sub-volume of the unit volume U_I for these droplets with equal radii can be estimated as $q(r_m) \cdot U_I$, also the number of droplets in each sub-volume consist of $N_m = 3q(r_m)U_I / (4\pi r_m^3)$. The total sum for the entire droplet intervals in all volumes of U_I are described by the following sum:

$$N = \frac{3AIT\beta}{4\pi} \sum_r \frac{q(r)}{r^3} \quad (9)$$

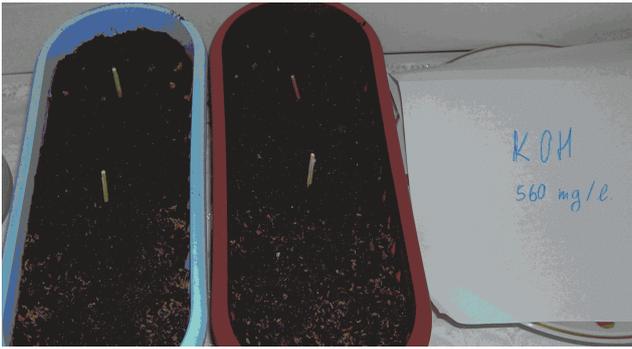
The calculations according to (9) provide the total number of falling droplets in mentioned water unit. For drizzle it is $N_d \approx 6.76 \cdot 10^{11}$, for rain $N_r \approx 4.02 \cdot 10^{11}$, and for storm $N_s \approx 2.45 \cdot 10^{11}$ for $AIT\beta = 3$ liters of water for drizzle, rain, or storm. These results prove that rain droplets could be interpreted as a porous medium with a large surface for gas/liquid interactions as compared to the ocean's plane surface. Then, each falling droplet runs at an air cylinder with a minimal volume length h and a ground area πr_m^2 . The cylinder surface $S_m \approx h2\pi r_m$ means that air/water interface increases for rainwater and purified air contact. The total sum of this surface for all droplets in considered water unit is, as follows:

$$S \approx \sum_r N_{m,I} S_m = \frac{3AIT\beta h}{2} \sum_r \frac{q(r)}{r^2} \quad (10)$$

The resulting calculations indicate that $S_d = 3.14 \cdot 10^8 \text{ m}^2$ for drizzle, that $S_r = 1.97 \cdot 10^8 \text{ m}^2$ for rain, and that $S_s = 1.25 \cdot 10^8 \text{ m}^2$ for storm, with the same units for a box of air volume under precipitation with a vertical altitude of $h = 1$ km and a background $A = 1 \text{ m}^2$ then $T = 1$ hour (then $I_1\beta_1=1$). As a result, the formula (10) demonstrates a great increase in air/water surfaces for purification possibilities as a result of rain. The rain consideration for drizzle, rain, or storms, with appropriate intensities $I = 3, 10$ or 30 mm/hour, are provided as example. Due to their linear contribution in formulas for N and S , the values of T, h, I , and A can be multiplied by any numeral for real time, altitude, or etc. The proposed algorithm indicates the principal possibilities for purification, and they could be developed, for example, to include no linear distributions for CO_2 , wind effects, etc.

Another advantage of the method relies on a substantial joint use of surface of all small droplets in the current precipitation volume. The joint set of water droplets increases the available surface for gas/liquid interactions. The corresponding calculations for expanded atmospheric air/water interface considering droplet set in precipitation volume with altitude $h_a = 1$ km and ground surface $A = 1 \text{ m}^2$ for precipitation time $T = 1$ hour provide the following numeric values: $S_d \approx 3 \cdot 10^8 \text{ m}^2$ for drizzle, $S_r \approx 2 \cdot 10^8 \text{ m}^2$ for rain, and $S_s \approx 10^8 \text{ m}^2$ for storm [21]. Due to the small CO_2 concentration in cloud media the probability of collision between water droplets and CO_2 molecules is low. The erosion of CO_2 as well as a significant decrease in its concentration occurs in the sub-cloud precipitation volume.

An extra advantage of proposed approach is the plant response to the precipitation. To emulate the process of CO_2 absorption in water droplets during an indoor experiment, the similar changes were made in alkaline solution during long-time diffusion according to formula $L \approx (Dt)^{1/2}$, a diffusion coefficient is $D = 10^{-5} \text{ cm}^2/\text{sec}$, but L is a water layer depth. The KOH was dissolved in water and resulting mixture was kept indoors during several hours $t = L^2/D$, as a result the solution has ions of $K^+; HCO_3^-; CO_3^{2-}$. The initial $pH=12$ was kept in these experiments. After saturation time t , the plants in brown pot were given the resulting solution and pure water was added to control blue pot (right side) with the same plants, Fig.1(a-e). These two watering processes were repeated regularly every day during January 2014. The experimental plants are beetroots (10 grains), carrots (20 grains), and parsley (2 grams) in each of plant pots, see Fig.1. The second experiment was done later with the same soil after deleting previous plants; the next portion as 20 grains of dill with 5 grains of cucumber were planted directly in both plant pots. The same watering process was repeated regularly every day during February 2014, results are presented at Fig.2. One can see a strong vegetation growth by enriched solution watering according to proposed method for all studied plants.



a



e

Figure 1(a-e). The indoor plants after 0 (a), 12 (b), 19 (c), 24 (d) and 31 (e) days correspondingly. The plants in a right (brown) flower pot were watered by solution with ions CO₃²⁻; HCO₃⁻; K⁺.



b



c



d



Figure 2. The next plants after 19 days in the same soils with the same watering procedures.

3. Results

In general the proposed method can be applied for the whole Earth on the global scale. The surface area of our planet is $A_E \approx 5,1 \cdot 10^8 \text{ km}^2$ and the average annual layer of precipitation is $h_w \approx 1,000 \text{ mm}$. Using equation (1) one can estimate the mass of removed atmospheric carbon (M_C^I) in 1 meter of precipitation water measured per surface 1 m^2 at $pH = 10 - 10,8$, for details see 1st and 2nd rows of Table. The estimated mass of CO₂ in 1 m^3 of water are presented at 3th row; the calculated mass of formed carbon at the surface of the whole planet is $M_C^A = M_C^I \cdot A_E = 0,849 \cdot 5,1 \cdot 10^{14} = 4,3 \cdot 10^{14} \text{ kg}$ then $pH = 10$, as listed at the 4th row of the Table. The carbon ratio in CO₂ is 0,2727, hence the amount of carbon oxide is $M_{CO_2}^A = M_C^A / 0,2727$ and its value listed at the 5th row of the Table. In 2010 the global CO₂ emission reached an amount of $3,06 \cdot 10^{13} \text{ kg}$. For further calculations let's assume the global annual emission of CO₂ $AE = 3,2 \cdot 10^{13} \text{ kg}$. To compensate an annual CO₂ emission from the ratio $AE / M_{CO_2}^A$ we estimate the minimal area at the Earth's surface (A_p , %) to be used for proposed technology and the corresponding details are given at the 6th row of the Table. For our approach the method has to be applied on 2% - 0,14% of planet surface. In general the proposed method can completely eliminate the annual carbon emission. To sum up

let's estimate the mass of alkali to add for desired modifications in clouds. The mass KOH (Q_{KOH}) can be estimated using previous data for n_{KOH} . Considering the precipitation layer of 1 m/year for the planet surface A its necessary percent ($\%A$) can be estimated from the Table. The added mass of alkali at $pH = 10$ level is calculated here:

$$Q_{KOH}^{10} = n_{KOH} \cdot l m \cdot A \cdot (A_p) = 5.6 \cdot 10^{-3} \cdot 1.5 \cdot 1 \cdot 10^{14} \cdot 0.02 = 5.7 \cdot 10^{10} \text{ kg} \quad (11)$$

Table 1. The carbon mass (M^A_c) and CO_2 mass ($M^A_{CO_2}$) for the Earth's surface $A = 5.1 \cdot 10^8 \text{ km}^2$; the minimal required surface (A_p) and mass of KOH (Q) to compensate an annual carbon emission.

1) pH -level	5.6	10	10.5	10.8
2) M_c^1 per 1 m^3 , kg	$1.6 \cdot 10^{-4}$	0.849	4.05	12.06
3) $M_{CO_2}^1$ per 1 m^3 , kg	$5.9 \cdot 10^{-4}$	3.11	14.8	44.2
4) $M^A_c = M_c^1 \cdot A$, kg	$8.2 \cdot 10^{10}$	$4.3 \cdot 10^{14}$	$2.1 \cdot 10^{15}$	$6.2 \cdot 10^{15}$
5) $M^A_{CO_2} = M_{CO_2}^1 \cdot A$, kg	$3 \cdot 10^{11}$	$1.6 \cdot 10^{15}$	$7.7 \cdot 10^{15}$	$2.3 \cdot 10^{16}$
6) A_p , %	-	2%	0.42%	0.14%
7) Q_{KOH} , mil. Tons	-	57	38	25

4. Conclusion

An approach for free atmosphere CO_2 purification is proposed that includes two simple stages. The first stage involves the injection of alkaline reagents into natural clouds in order to increase their pH -level up to 10 or 11. Precipitation enhancement proposes for the carbon transport from atmosphere to the ground. It was shown by corresponding calculations that there is a considerable increase of the gas/water interface; at such surface one can observe the ensemble of all rain droplets with fast CO_2 absorption. The result effect can compensate for annual carbon emission by method application at 0.42% – 0.14% of the Earth surface. The proposed idea can be developed further to get an effective technology for atmosphere purification and climate recovery as a result.

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